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FOR Mg, Al, and Si USING PURE-ELEMENT STANDARDS¹

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ABSTRACT

Accurate electron probe values for Mg, Al, and Si in silicate minerals may be obtained with pure-element standards. Analysis must be done at low (6 kV) accelerating potential and, for best results, the average atomic number of the sample should be within about ± 1 of the atomic number of the pure-element standard. This last requirement is automatically fulfilled for most common silicate minerals, as their average atomic numbers usually fall within the 11 to 15 range.

Examples studied include a wet-chemically analyzed cordierite containing 17.71 weight percent Al, for which a value of 17.6 ± 0.3 percent was obtained with the electron probe, and a hornblende containing 19.15 percent Si, which gave 19.0 ± 0.3 percent using the probe method.

¹Portions of this paper were presented at the 7th National Conference of the Electron Probe Analysis Society of America, July 17–21, 1972, San Francisco, California.

INTRODUCTION

The present work is an extension of studies by Desborough and Heidel (1971). Using wet-chemically analyzed silicate standards, they found that matrix-effect corrections are reduced or eliminated at 6 keV as compared to the more energetic 15 or 20 keV excitation conditions commonly employed in electron probe analysis. The improved data are the result of shallower electron penetration, which gives rise to shallower depth of generation of the analytical X-rays, reducing the path length over which the X-rays must travel in the sample. We show here that using pure-element standards without matrix-effect corrections, satisfactory results can be obtained for silicon, aluminum, and magnesium in most silicate minerals, provided analysis is done at the low (6 kV) accelerating potential.

EXPERIMENTAL

A Materials Analysis Company Model 400 electron probe was used; this unit has the sample inclined, resulting in electron beam impact 27.5 degrees from the normal to the sample surface; takeoff angle is 35 degrees. The probe was operated at a sample current of 0.01 microamp with an ADP crystal and a flow proportional detector (P-10 gas). Count rates were relatively low: 100 counts per second. Beam size was 5 microns. Pure Si, and Al, and Mg, obtained from commercial sources, were used as standards. Four analyzed silicate minerals, sufficiently well characterized by wet chemistry as to be in use as primary standards in a number of electron probe laboratories, were test samples in determining the accuracy of the method. The analyzed minerals were selected so as to represent a wide range of matrices, compositions and average atomic numbers. Synthetic quartz and corundum were also used as test samples. Wavelength shifts, although minor under the

conditions employed, were carefully determined and taken account of in making the measurements. Instrumental corrections (drift, background and deadtime) were made when necessary, but nowhere were matrix-effect corrections applied. Ten different grains or areas of sample (where the latter was a single large fragment) were analyzed, three 50-second counting periods being taken on three separate locations on each grain (or area).

RESULTS

The data are in Table 1. The analyzed mineral samples are arranged in increasing atomic number from left to right, and the pure-element standards are at the left in column 1. Where the atomic number of silicate sample is different from the pure-element standard (as in quartz analyzed with pure silicon, column 3, bottom) the electron probe data are not in agreement with the wet-chemical values. In contrast, if atomic number of the standard is near that of the sample, as is the case with Al in Wilburforce hornblende (column 6), quite accurate results are obtained using the pure-element standards. It is clear from Table 1 that best results are obtained if the atomic number of the standard is within about ± 1 of the average atomic number of the sample. As the average atomic number of most common silicates ranges from 11 to 15, the pure-element standards will at 6 keV be effective for a large number of these minerals.

Some modifications might be made to the analytical approach used by us, perhaps with some improvement in precision and accuracy. To adjust for the atomic number effect in cases where this becomes necessary, electron-retardation (stopping-power) corrections, such as the simple one proposed by Frazer et al. (1971) could be calculated. If either KAP or RbAP crystals were employed, instead of the less-efficient ADP crystal we used, peak-to-background ratios could probably be

greatly increased. In addition, accelerating potential could probably be lowered. We point out that the choice of 6 kV does not appear to be especially critical: Frazer et al. (1971) have shown that as accelerating potential is lowered to a level approaching the excitation potential of the element of interest, matrix effects—except for the atomic number effect—approach zero. Therefore, accelerating potential could be reduced to a value closer to the excitation potentials of Si (1.74 keV), Mg (1.25 keV) or Al (1.47 keV) and further improvement over the 6 keV results would presumably be obtained. Unless counting time and sample current were increased, however, this would be done at the sacrifice of precision owing to reduction of the already low 6 keV count rate. The 6 kV approach provides sufficient overvoltage to allow reasonably efficient count rates, yet is low enough to greatly reduce absorption and fluorescence corrections.

Although they are relatively low in energy, the 6 keV electrons and the emergent analytical X-rays did not seem to be much affected by varying thicknesses of carbon coat or possible oxidation of the pure element standards. As verification of this we determined the accelerating potential at which an 8000Å Al foil would just pass electrons. At 7.8 kV the foil stopped all electrons; above that potential, electrons penetrated the foil. This thickness is large enough, and the accelerating potential concerned sufficiently similar to the 6 keV used in the measurements, that we suggest even a 1000Å thick carbon coat combined with a 500Å thick oxide layer on the pure-element standards would not influence the results. It is recommended, however, that reasonable care be used with the standards: thin carbon coating soon after polishing, together with storage in desiccators.

DISCUSSION

The method as described and used above has several advantages. Only the element(s) of interest need be analyzed; most procedures require determination of the total matrix in order to correct for inter-element effects, even if data are required on only one element in the sample. Size of the library of analyzed mineral standards required to perform analysis is reduced, as is computer correction time. The latter advantages may apply mainly to beginning laboratories. But conceivably more well-established probe users could find the method useful for checking compositions of silicate standards, or for verifying computer-corrected silicate results, in cases where the latter have undergone large corrections.

The low keV method does, however, have several disadvantages. Owing to lower count rates, longer counting time is required to maintain precision. Reduced electron penetration may prove to be a drawback if surface contamination or irregularity of sample surfaces occurs. In addition, we have on occasion found instrumental instability (changing count rates, beam wandering) to be a problem at the lower accelerating potential, more so than at, say, 20 or 25 keV. This effect may only be a function of the particular instrument, and workers trying the method may find their own units to be more stable.

Despite these possible difficulties, we recommend the 6 keV pure-element standardization method for silicates as being simple, rapid and accurate, where average atomic number of the sample is near the atomic number of the standard.

REFERENCES

- Desborough, G. A., and R. N. Heidel (1971) Improved electron microprobe analysis at low operating voltage: I. Silicon, magnesium and aluminum. Am. Mineral. 56, 2129-2135.
- Frazer, Jane Z., H. Fujita, and R. W. Fitzgerald (1971) A new procedure for quantitative X-ray analysis with electron excitation. Mat. Res. Bull. 6, 711-724.

TABLE 1. SIX keV ANALYSIS OF MINERALS FOR Mg, Al, and Si
USING PURE-ELEMENT STANDARDS WITH M.A.C. PROBE

Pure- Element Standard	Mineral	Corundum $\bar{Z} = 10.65^a$	Quartz $\bar{Z} = 10.80$	Cordierite $\bar{Z} = 10.97$	Marjalahti Olivine $\bar{Z} = 11.90$	Wilburforce Hornblende $\bar{Z} = 13.80$	Suzimaki Olivine $\bar{Z} = 14.98$
Mg (Z = 12)							
Chemical ^b		—	—	7.27	28.60	5.02	15.40
Microprobe ^c		—	—	7.1±0.3	28.5±0.8	4.8±0.3	14.5±0.5
Al (Z = 13)							
Chemical		52.92	—	17.71	—	5.11	—
Microprobe		52.7±0.6	—	17.6±0.3	—	5.1±0.4	—
Si (Z = 14)							
Chemical		—	46.76	23.07	18.83	19.15	16.50
Microprobe		—	44.9±0.6	19.4±0.4	18.6±0.2	19.0±0.3	16.9±0.5

^a \bar{Z} : Average atomic number ($= \sum C_i Z_i$, where C = weight fraction, Z = atomic number).

^bChemical: Wet chemical values, weight percent of element.

^cMicroprobe: Microprobe results uncorrected for matrix effects.

^dStandard deviation for 10 sample grains or areas of sample. Horizontal lines indicate elements not present or not determined (below 0.2% weight percent of the element).